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May 23, 2008

ACS NANO

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Effect of order in self-assembled monolayers on the orientation of poly(3-hexylthiophene) crystallites

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Abstract:

Molecular dynamics simulations are used to study the influence of the molecular properties of chemically functionalized substrates on the orientation of poly(3-hexylthiophene) (P3HT) crystallites. The effects of alkyl-trichlorosilane self-assembled monolayer packing density, packing order, and end-group functionality are independently, and parametrically investigated. From these simulations, the potential energy surface presented by the substrate to the P3HT molecules is determined to be the main driver of P3HT ordering. Disordered substrates with a smoothly varying potential energy landscape are found to encourage ideal edge-on P3HT orientation for thin-film transistor applications; highly ordered substrates with undesirable periodic potential energy wells are found to trap a fraction of P3HT side chains out of their natural geometry and hence disrupt favorable ordering.

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Organic electronic devices are being actively investigated for application areas where the use of conventional Si-based devices is impractical, too expensive or impossible, such as solution-coated large-area solar cells and inkjet-printable electronic circuits. One of the most studied semiconductors for organic thin-film transistors (OTFTs) is poly-3-hexylthiophene (P3HT). P3HT is solution-processable, exhibits a relatively high charge carrier mobility ($> 0.1\text{cm}^2/\text{V.s}$)¹ and is commercially available. When cast from solvents into thin films, P3HT has a semicrystalline microstructure comprised of nanoscale (10-50 nm) crystallites and amorphous regions. The performance of P3HT OTFTs is strongly affected by the microstructure of the semiconductor layer.^{2,3} A key factor in determining the microstructure of P3HT is the nature of the semiconductor/dielectric interface, where the P3HT crystallites nucleate upon film formation.^{4,5} The link between OTFT morphology and charge carrier mobility has been recently studied experimentally.⁶ The highest charge carrier mobility in the plane of the substrate is observed when both the alkyl chains and the thiophene rings of the P3HT crystallites are normal to the substrate surface (edge-on orientation).^{1,2,7}

Previous work has found that chemically modifying a typical substrate (SiO_2 thermally grown on a Si wafer) with a self-assembled monolayer (SAM) of octadecyltrichlorosilane (OTS) substantially enhances the device performance of most polymeric semiconductors.^{5,8} X-ray rocking curves indicate that the angular spread of the edge-on crystallites about the substrate normal plays an important role in charge transport: the smaller the spread, the better the intergrain electronic coupling. For instance, treating the dielectric surface with OTS produced a population of P3HT crystallites oriented within an angular spread smaller than 0.03° (limited by the resolution of the rocking curve measurement) up to one order of magnitude larger than that produced on hexamethyldisilazane (HMDS) treated surfaces.⁵ However, the mechanisms by which the SAMs interact with the polymer are unknown and difficult to characterize due to the buried nature of that interface. Such understanding is of fundamental importance in order to optimize the design and the processing of SAMs and control the microstructure of the polymeric semiconductor with the goal of achieving the best possible electronic properties. In this work we use P3HT as a model polymeric semiconductor to examine,

for the first time using computational tools, the problem of engineering P3HT morphology through controlling the interactions between P3HT and the substrate.

Given that the relative orientation of the polymer crystallites plays such an important role in charge transport, the objective of this work is to identify some of the most important substrate properties that affect such orientation. On an ideal OTS-treated substrate, the OTS molecules are nearly fully extended⁹ and packed at a high density of roughly 5 chains per nm²,^{10,11} screening the effects of the substrate below. Moreover, when perfectly ordered, the OTS molecules are close-packed on the surface, exhibiting long-range order, in contrast to amorphous silica.^{11,12} Finally, the CH₃ termination of the OTS molecules might impact how the P3HT chains pack. Table 1 describes the parameters defining the alkyl-trichlorosilane SAM layer that were varied in the simulations, namely, density, packing order, and end group functionality. A packing order value of 0.33, for example, indicates that 67% of the SAM molecules are randomly displaced from their equilibrium positions in the plane of the substrate by an amount equal to at most half the packing distance in the plane of the substrate. Displaced molecules are then allowed to relax to obtain the final surface.

This study investigates the significance of each of these three parameters. To this end, we have performed classical molecular dynamics (MD) simulations, and employ the COMPASS forcefield¹³ for all atom-atom interactions. All MD simulations were carried out using the LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) code¹⁴ under constant particle number, volume, and temperature (*NVT*) conditions at a temperature of 300K, using three-dimensional periodic boundary conditions. The equations of motion were integrated using the Verlet algorithm¹⁵ with a time step of 1.0 *fs*. The nonbonded van der Waals interactions were treated by truncating atom pairs with an inter-atomic distance greater than $r_c=15\text{\AA}$, coupled with a long-range tail correction.¹⁶ The particle-particle particle-mesh Ewald (PPPM) method¹⁷ was used for the long-range treatment of electrostatic interactions with a k-space accuracy set at 10⁻⁵. Fig. 1 illustrates the simulation geometry; with periodic boundaries and near-ideal registry between neighboring images, the computations closely represent P3HT crystallites such as those that would be found near the substrate surface in a thin film.

The initial P3HT configuration (Fig. 1a) is chosen to be very similar to the

nanocrystallites of edge-on oriented low-molecular weight (MW) P3HT observed at the OTS-P3HT interface by Kline *et al.*⁵ The key figure of merit considered here is the mean order parameter, $\langle S \rangle$, averaged over all 608 side chain vectors every 1000 timesteps. $\langle S \rangle$ is given by

$$\langle S \rangle = \left(\sum_i \frac{3 \cos^2 \theta_i - 1}{2} \right) / n_{\text{side chains}} \quad (1),$$

where θ_i is the angle between a single side chain i and the substrate normal and n is the total number of side chains. Side chain vectors point from the S atom on each thiophene ring to the terminal CH₃ or CF₃ group on the corresponding alkyl chain. $\langle S \rangle = 1$ thus corresponds to perfect edge-on orientation and $\langle S \rangle = -0.5$ corresponds to face-on orientation (see Fig. 1 inset).

All systems studied seemed to equilibrate with respect to $\langle S \rangle$ in under 0.5 ns; however, in order to confirm that equilibration had indeed taken place, several representative simulations were run for at least 1 ns each. We find that our results can be separated in three distinct side chain order regimes (see Table 1): (1) $\langle S \rangle$ larger than 0.6 (high orientational order); (2) $\langle S \rangle$ between 0.6 and 0.5 (intermediate orientational order); and (3) $\langle S \rangle$ smaller than 0.5 (low orientational order). Disordered SAMs generate the highest $\langle S \rangle$ values, followed by the ordered fluorinated SAMs.

In general, the order parameters of the P3HT oligomers listed in Table 1 are related to the level of molecular order in the underlying substrate surface. The ordered OTS monolayers, for the CH₃ and CF₃ end group chemistries considered here, produce the lowest degree of edge-on orientation in the P3HT crystallites, while disordered substrates correlate with increased P3HT orientational order (e.g., larger values of $\langle S \rangle$). Several potential explanations for these results were ruled out; first, annealing and cooling simulations show that the ordering is not driven by the thermal motion of the OTS or the side chains. Second, the *trans:gauche* ratios of the P3HT side chains do not vary with changes in the order parameter. Instead, the key difference between ordered and disordered substrates is that highly ordered SAMs present disruptive periodic energy minima to P3HT molecules.

As illustrated in Fig. 2, the gaps between perfectly packed OTS chains serve as potential energy wells for P3HT side chains, even though they are not large enough to permit interdigitation (which occurs only when the SAM is not fully dense). The energy displayed in Fig. 2 represents the per-atom potential energy of the terminal C atoms on the P3HT side chains as they interact with the substrate; reported energy is the sum of pair, bond, angle, dihedral, and improper terms. The regular lattice-like spacing of the potential energy wells in the ordered SAMs considered here is incommensurate with the edge-on side chain spacing in P3HT and hence hinders perfect edge-on orientation. This effect occurred whether the SAM molecules were all CH₃-terminated, all CF₃-terminated, or had mixed end groups. The extended deep potential energy wells and sharp energy peaks presented to the P3HT side chains by a well-ordered substrate can be seen in Fig. 2. The perfectly packed OTS molecules are very restricted in their motion and remain close to their original lattice sites, shown in the figure as black dots. Low potential energy regions correspond to interstitial spaces between OTS close-packed directions, and high potential energies occur on or near OTS sites where side chain terminal groups collide with the CH₃ groups on the OTS molecules. The three trajectories in the figure demonstrate that the P3HT side chains tend to linger in the energy wells and move abruptly away from regions of high potential energy.

The effects of partially disordered (i.e., 33% and 67% disordered) SAMs were more complex; these simulations showed the greatest fluctuations in their order parameters. The fluctuations can be correlated with local variations in the surface potential, which in turn depended on how the OTS molecules had been randomly perturbed from perfect packing in the simulation setup. The influence of the local differences in surface potential that existed in the partially disordered simulations is shown in Fig. 3. Fig. 3a suggests that P3HT morphology is strongly dependent on local substrate surface potential. The value of the orientational order parameter $\langle S \rangle$ for all P3HT side chains decreases sharply at approximately 620 *ps* after the beginning of the simulation, driven by those at the surface. At 825 *ps*, the order parameter for surface side chains increases dramatically, and the rest of the P3HT crystal trends towards greater order as well. This surface-mediated disordering and ordering is especially noteworthy since the near-surface P3HT side chains were only a small fraction of the total, and

entered into the total $\langle S \rangle$ calculation accordingly. Figs. 3b and 3c examine side chain potential energies at these times of relatively low and high surface side chain order, respectively. Similar to Fig. 2, Fig. 3b exhibits wide regions of extremely low potential energy and relatively steep gradients, which correlate with low P3HT orientational order. Fig. 3c, in contrast, has generally higher potential energy, with no deep potential energy wells, and more gentle gradients, hinting at greater substrate disorder. The end groups of the SAM molecules in these more disordered parts of the substrate are more mobile, oscillating far from their initial positions over time and presenting a relatively even surface of higher potential energy to the P3HT side chains. P3HT in contact with a surface of that nature displayed greater order.

The cases in which P3HT was placed on a completely disordered SAMs or on a bare amorphous SiO_2 surface gave the most stable edge-on orientation of the crystallites. Fig. 4 shows near-surface P3HT side chain potential energies on a bare SiO_2 substrate, which produced a high average order parameter $\langle S \rangle$. The surface potential, as experienced by P3HT side chain terminal C atoms, is generally high, with only small energy wells. The energy wells are bounded by potential peaks, which screen their trapping effect on P3HT side chains. Thus, the bare SiO_2 surface does not show evidence of a high density of sites that can strongly attract the P3HT side chains and disturb the P3HT orientation.

This computational study indicates that the potential energy landscape created by the substrate for P3HT side chains governs the orientation of the polymer molecules. Perfectly ordered crystal-like substrates with periodic potentials disrupt the ideal P3HT edge-on orientation. The disordered substrates considered here, which have energetically smoother and generally higher-potential energy surfaces, encourage P3HT crystallite orientation closer to the ideal edge-on texture. High energy substrates may be desirable as well since they would tend to minimize P3HT side chain contact, thus favoring edge-on orientation. It should be added however that from a practical standpoint, high-energy substrates may be undesirable because they are more susceptible to contamination. Another interesting case would involve a substrate coated with a highly ordered SAM that has a spacing in the close-packed direction close to twice the length of a P3HT monomer, which might generate a sort of “side chain epitaxy” that allows side chains to

lock into substrate energy wells in their natural geometry. Additionally, a chemically mixed multilayer might provide packing irregularities that would ultimately encourage edge-on P3HT alignment.

Acknowledgements

This work is performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

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TABLE 1. Simulation names and results. Density=1.0 corresponds to 5 OTS molecules nm⁻². Order=1.0 is perfect hexagonal packing. Fluorination=1.0 is 100% SAM termination with CF₃ groups instead of CH₃. Reported $\langle S \rangle$ values are averages over final 100 *ps* at intervals of 1 *ps* (final 20 *ps* for the shorter runs). Trials with * next to their $\langle S \rangle$ values exhibited interdigitation among the P3HT side chains and the SAM molecules.

Trial Name	SAM density	SAM order	SAM fluorine fraction	order parameter $\langle S \rangle$ (value/stdev)	simulation time (ns)
perfect_layer	1.0	1.0	0.0	low (0.47/0.013)	1.012
dens_75	0.75	1.0	0.0	low* (0.49/0.0095)	1.097
dens_50	0.5	1.0	0.0	low* (0.44/0.010)	0.186
bare_substrate	0.0 (no SAM)	N/A	N/A	high (0.69/0.0095)	1.002
order_66	1.0	0.66	0.0	high (0.70/0.0093)	2.999
order_33	1.0	0.33	0.0	low (0.48/0.013)	1.345
order_0	1.0	0.0	0.0	high (0.70/0.014)	1.044
fluor_25	1.0	1.0	0.25	medium (0.54/0.012)	0.175
fluor_50	1.0	1.0	0.50	medium (0.55/0.0098)	0.358
fluor_100	1.0	1.0	1.0	medium (0.55/0.0097)	1.010
control	P3HT only	N/A	N/A	low (0.45/0.0086)	0.423

List of Figure Captions:

FIG. 1. (a) Initial simulation geometry, prior to any simulation time. An edge-on P3HT crystal equilibrated in isolation under NPT conditions ($T=300$ K) and consisting of $2 \times 8 \times 2$ 19-mers is placed in contact with an amorphous silica substrate and a SAM with a maximum of 240 OTS molecules. Visualization created with Qutemol.¹⁸ (b) An example of an equilibrated simulation (order_66 from Table 1) after 2.999 *ns* of dynamics. Some P3HT backbones appear to be divided because they passed through a periodic boundary and appeared on the other side of the simulation cell.

FIG. 2. XY projection of typical per-atom potential energies (pair, bond, angle, dihedral, and improper contributions) of P3HT side chain terminal C atoms that are nearest the OTS surface in the perfect_layer simulation. The three darker lines are trajectories for three individual C atoms. Black dots are the nominal positions of OTS molecules. These perfectly packed molecules create disruptive periodic energy minima for the P3HT side chains. Scale bar is 1 nm. Units of energy are kcal/mol.

FIG. 3. (a) Evolution in time of side chain order parameters for the order_33 simulation. The total $\langle S \rangle$ is separated into contributions from side chains closest to the substrate, between the two layers of P3HT molecules, and at the top of the simulation box. (b) Surface potential energies of the terminal side chain C atoms from 625 *ps* to 641 *ps* in Fig. 3a, where $\langle S \rangle$ is low. Same quantity as (b) plotted from 884 *ps* to 900 *ps*, when $\langle S \rangle$ is high (c). Scale bars are 1 nm. Units of energy are kcal/mol.

FIG. 4. Surface potential energies of terminal side chain C atoms in the bare substrate simulations. Scale bar is 1 nm. Units of energy are kcal/mol.

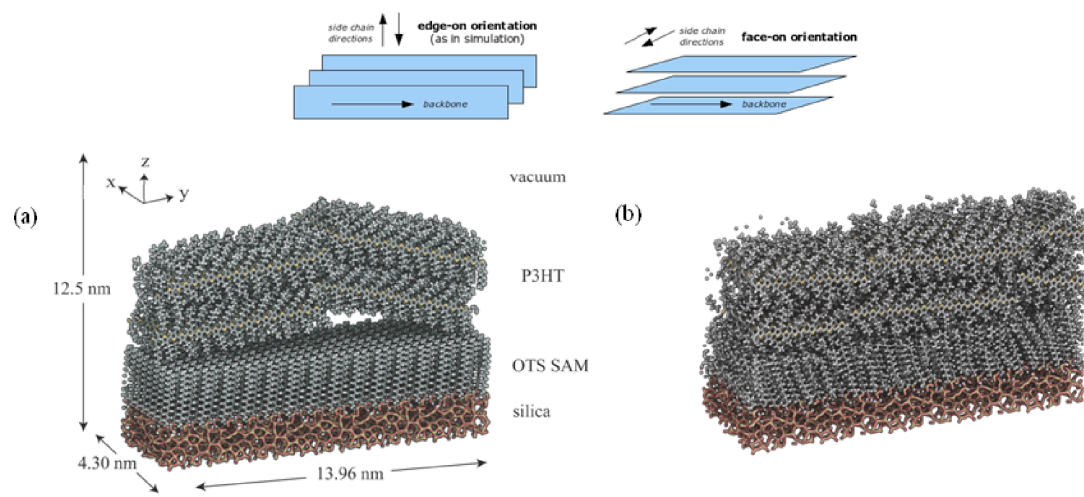


FIG. 1.

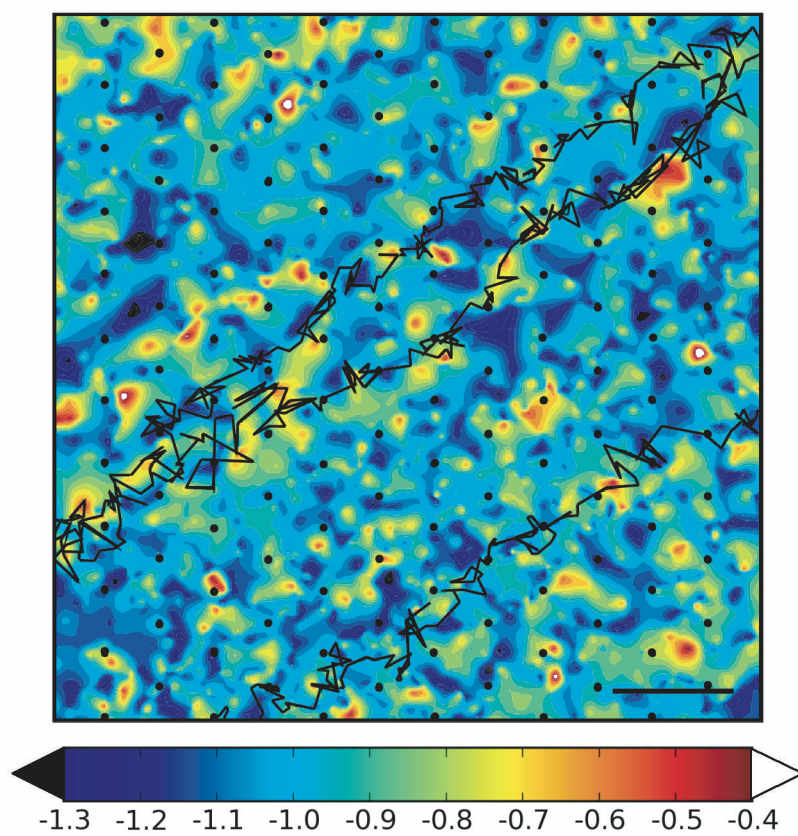


FIG. 2.

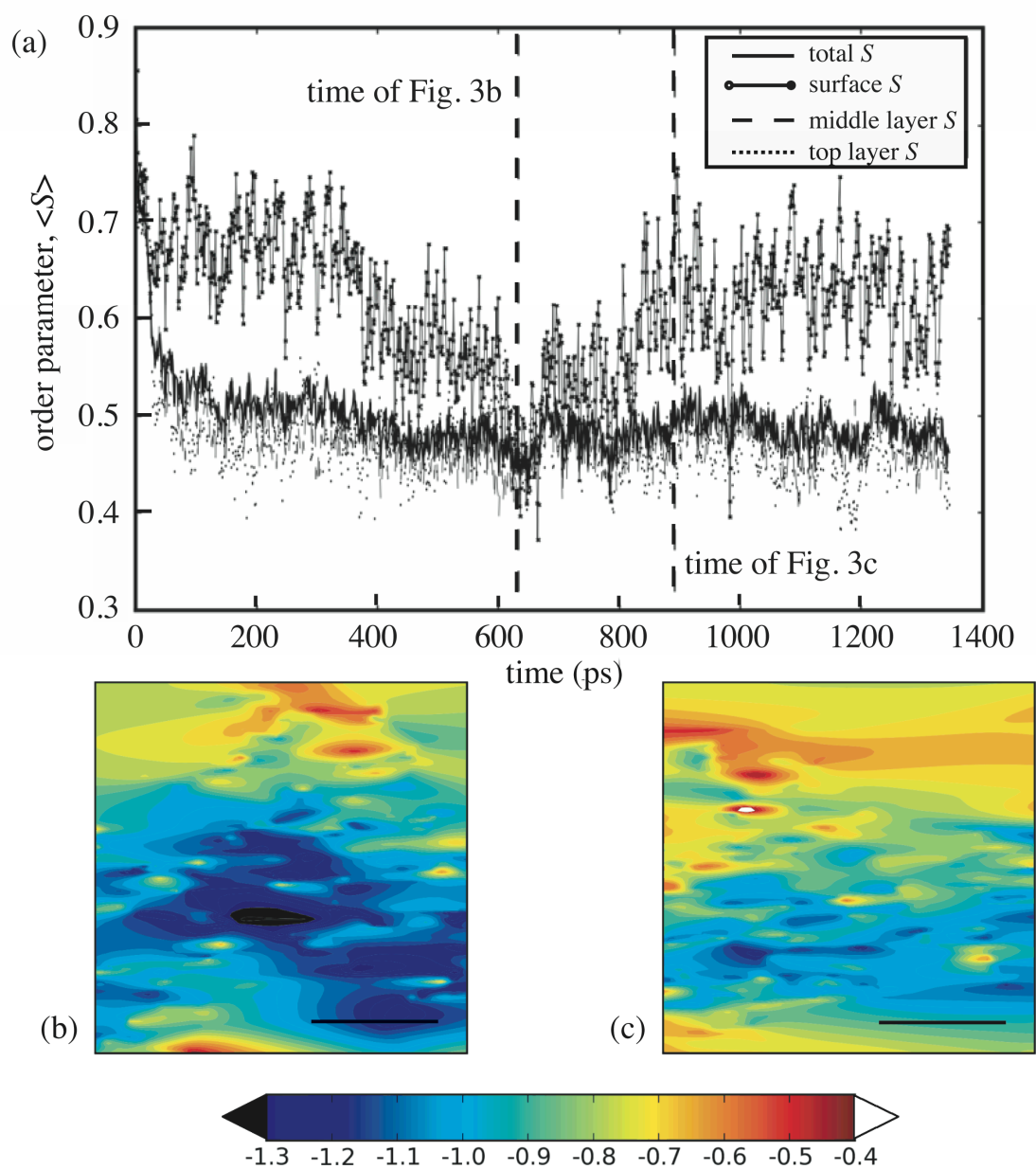


FIG. 3.

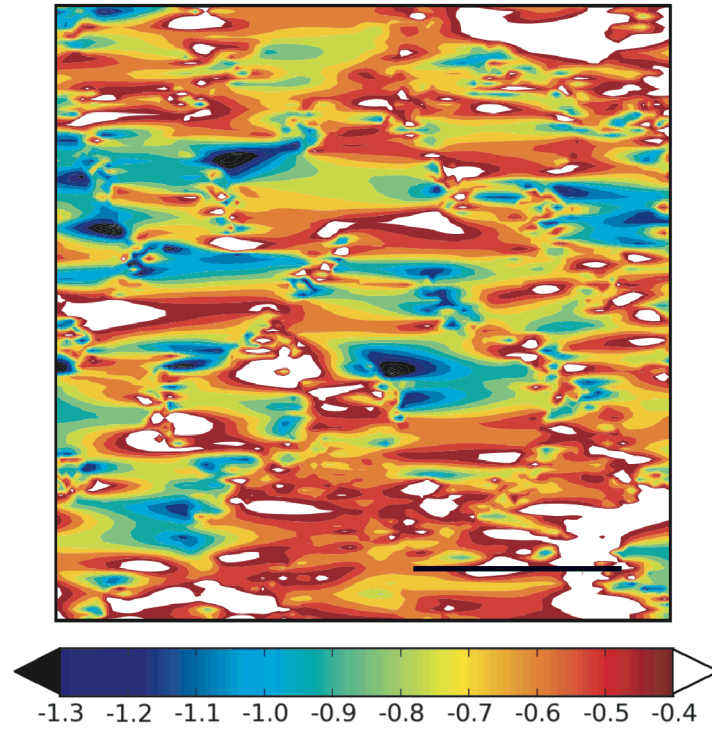


FIG. 4.